Determination of the organic aerosol mass to organic carbon ratio in IMPROVE samples

Hazem S. El-Zanan [a], Douglas H. Lowenthal [a,*], Barbara Zielinska [a],
Judith C. Chow [a], Naresh Kumar [b]

[a] *Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, USA*
[b] *EPRI, 3412 Hillview Avenue, Palo Alto, CA 94303, USA*

Abstract

The ratio of organic mass (OM) to organic carbon (OC) in $PM_{2.5}$ aerosols at US national parks in the IMPROVE network was estimated experimentally from solvent extraction of sample filters and from the difference between $PM_{2.5}$ mass and chemical constituents other than OC (mass balance) in IMPROVE samples from 1988 to 2003. Archived IMPROVE filters from five IMPROVE sites were extracted with dichloromethane (DCM), acetone and water. The extract residues were weighed to determine OM and analyzed for OC by thermal optical reflectance (TOR). On average, successive extracts of DCM, acetone, and water contained 64%, 21%, and 15%, respectively, of the extractable OC, respectively. On average, the non-blank-corrected recovery of the OC initially measured in these samples by TOR was $115 \pm 42\%$. OM/OC ratios from the combined DCM and acetone extracts averaged 1.92 and ranged from 1.58 at Indian Gardens, AZ in the Grand Canyon to 2.58 at Mount Rainier, WA. The average OM/OC ratio determined by mass balance was 2.07 across the IMPROVE network. The sensitivity of this ratio to assumptions concerning sulfate neutralization, water uptake by hygroscopic species, soil mass, and nitrate volatilization were evaluated. These results suggest that the value of 1.4 for the OM/OC ratio commonly used for mass and light extinction reconstruction in IMPROVE is too low.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Aerosol; Extraction; OC conversion factor; Mass balance

1. Introduction

Carbonaceous species such as black carbon (BC) and organic carbon (OC) constitute a significant portion of the atmospheric aerosol mass in urban and rural areas of the US (Malm et al., 1994, 2004; Chow et al., 1994a,b; Novakov et al., 1997; Andrews et al., 2000). Because of analytical limitations, only about 20% of the organic fraction has been specifically identified (Sempere and Kawamura, 1994; Saxena and Hildemann, 1996; Turpin et al., 2000). Methods for determining bulk OC and BC are based on thermal and thermal–optical techniques (Novakov, 1982; Cachier et al., 1989; Chow et al., 1993, 2001; Birch and Cary, 1996). One of the disadvantages of these methods is their inability to measure species other than carbon such as oxygen, hydrogen,

---

nitrogen, sulfur, chlorine, and other elements associated with organic matter.

Accurate determination of OM from bulk OC measurements is needed for applications such as source apportionment that require mass closure and to estimate physical properties such as aerosol light extinction from its chemical components. The IMPROVE (Interagency Monitoring of PROtected Visual Environments) network was established to monitor visibility and aerosol chemistry in national parks and remote areas around the US. $PM_{2.5}$ (particles with diameters smaller than 2.5 μm) mass concentration at IMPROVE sites has been reconstructed as the sum of sulfate as $(NH_4)_2SO_4$ (AMSUL), nitrate as NH_4NO_3 (AMNIT), organic matter (OM) as 1.4 times OC, elemental carbon (EC, defined as equivalent to BC), and soil dust (Malm, 2000; Watson, 2002a):

$$PM_{2.5}\ Mass = AMSUL + AMNIT + OM + EC + Soil \tag{1}$$

The soil dust concentration is expressed as the modified sum of the oxides of the major crustal elements, expressed in their most oxidized form:

$$Soil = 2.2Al + 2.49Si + 1.63Ca + 2.42Fe + 1.94Ti \tag{2}$$

This approach has been adopted for estimating light extinction for compliance under the US Environmental Protection Agency's Regional Haze Rule (USEPA, 2001). A factor of 1.4 is used in the "IMPROVE equation" to convert OC to organic mass (OM) to account for unmeasured species in OM. This factor is the ratio of OM/OC, i.e., the average molecular weight per carbon weight for the organic material. The value of 1.4 was based on an experiment conducted by Grosjean and Friedlander (1975), who collected samples at Caltech, Pasadena on six different days in 1973. They found that the carbon content of these samples ranged from 67% for the polar organic fractions to 85% for the non-polar fractions with an average of 73%. White and Roberts (1977) based an OC to OM conversion factor of 1.4 on the reciprocal of 0.73. Countess et al. (1980) derived an OM/OC ratio of 1.2 from Van Vaeck and Van Cauwenberghe (1978), who reported ratios of 1.17, 1.30, and 1.08 for aliphatic hydrocarbons, carboxylic acids, and polynuclear aromatic hydrocarbons, respectively, in aerosol particles. Turpin and Lim (2001) recommended the use of an average organic molecular weight per carbon weight ratio of 1.6 ± 0.2 and 2.1 ± 0.2 for urban and non-urban aerosol, respectively, based on analysis of samples collected at four Los Angeles Basin locations by Rogge et al. (1993).

The average OM/OC ratio is expected to increase as aerosols age during transport. Photochemical reactions produce secondary organic compounds that are more oxygenated than their primary precursors. Thus, the OM/OC ratio is likely to be higher at rural sites downwind of sources in urban areas. Hegg et al. (1997) used a factor of 1.7 to convert OC to OM during the TARFOX experiment, which examined the evolution of aerosols transported from the US east coast over the Atlantic Ocean. Krivácsy et al. (2001) isolated the water-soluble organic carbon (WSOC) fraction of aerosols from the Jungfraujoch, Switzerland using solid phase extraction. A WSOC OM/OC ratio of 1.91 was inferred from elemental composition (C, N, H, and S) measured with a Carlo Erba CHNS–O 1108 elemental analyzer and mass determined with a Sartorius ultra-microbalance. Kiss et al. (2002) used the same technique to estimate an OM/OC ratio of 1.93 for WSOC in fine aerosols from K-puszta, a rural site in Hungary. Russell (2003) used FTIR (Fourier Transformed Infrared) spectroscopy to estimate the OM/OC ratio. This approach estimates composite organic carbon from the number of carbon bonds present and the organic mass from the functional group mass associated with each measured bond type. The derived ratios for sub-micron aerosol particles collected during ACE (Aerosol Characterization Experiment)—Asia in the western Pacific and PELTI (Passing Efficiency of the Low Turbulence Inlet Experiment) in the Caribbean were between 1.2 and 1.6, averaging about 1.4. The significance of these results for relatively remote marine locations is that they are similar to those expected for urban environments.

Andrews et al. (2000) evaluated mass closure during SEAVS (Southeastern Aerosol and Visibility Study) at Great Smoky Mountains National Park during the summer of 1995. They found that only 64% of measured $PM_{2.5}$ was accounted for by the sum of IMPROVE sampler sulfate, nitrate, ammonium, EC, OM, and soil. Andrews et al. (2000) attempted to explain the reconstructed mass deficit in terms of underestimation of the fine soil component, weighing artifacts, and underestimation of OM. They concluded that the fine soil contribution was too small to account for deficits in reconstructed mass and that the assumed OM/OC ratio of 1.4 may be too low.

Lowenthal and Kumar (2003) examined $PM_{2.5}$ mass closure at IMPROVE sites based on Eq. (1). $PM_{2.5}$ mass was systematically underestimated across the IMPROVE network. Measured and reconstructed mass agreed more closely when major elements including Na and Cl and trace elements were added to Eq. (1). Lowenthal and Kumar (2003) concluded that the remaining mass deficit was related to uncertainties in the OC measurement and the assumed OM/OC ratio.

In this paper, the OM/OC ratio at IMPROVE sites was estimated using two approaches: (1) direct measurement of the OM mass and carbon content of solvent extracts of archived IMPROVE filter samples; and (2) mass balance analysis of measured $PM_{2.5}$ and chemical concentrations in thousands of samples from the IMPROVE network.

2. Experimental

IMPROVE samples of 24-h duration are collected every third day. The IMPROVE sampler consists of four modules (Malm et al., 1994, 2004; Malm, 2000). Modules A, B, and C are preceded by $PM_{2.5}$ size-selective inlets. Module A contains a Teflon filter for measurement of mass and elements. Module B contains a nylon filter preceded by an annular anodized aluminum nitric acid denuder coated with Na_2CO_3 for measurement of nitrate, nitrite, sulfate, and chloride. Ashbaugh et al. (2004) reported that the denuder is highly effective and efficient at removing nitric acid but that the aluminum surfaces of an un-denuded sampler inlet are just as efficient. Organic and elemental carbon (OC and EC) are measured on quartz–fiber filters in module C. A quartz backup filter for each sample was originally used to estimate the amount of volatile organic carbon (VOC) absorbed by the front quartz–fiber filter (Turpin et al., 1994). After it was recognized that both the backup filters and dynamic field blanks become saturated with VOC, the median OC concentration on backup filters from six sites during a calendar quarter was used as the dynamic OC field blank for that quarter for all samples at all sites in the network. (Watson, 2002a). IMPROVE samples are routinely analyzed for OC and EC by TOR following the IMPROVE protocol (Chow et al., 1993) at the Desert Research Institute (DRI) and archived in freezers. Module D is preceded by a PM_{10} size-selective inlet and contains a Teflon filter for measurement of PM_{10} mass concentration.

Archived IMPROVE quartz filters were selected from five regionally representative national parks shown in Fig. 1: Acadia (ACAD), ME, Great Smoky Mountains (GRSM), TN, Big Bend (BIBE), TX, Indian Gardens (INGA), Grand Canyon, AZ, and Mount Rainier

Fig. 1. Locations of Acadia National Park, ME (ACAD1), Great Smoky Mountains National Park, TN (GRSM1), Big Bend National Park, TN (BIBE1), Indian Gardens, Grand Canyon National Park, AZ (INGA1), and Mount Rainier National Park, WA (MORA1).

(MORA), WA from 1998 through 2000. For each site, 0.5 cm^2 punches taken from each archived filter were composited by season: summer (SM) = June, July, August; fall (FL) = September, October, November; winter (WN) = December, January, February; and spring (SR) = March, April, May. Each season represented approximately 30, 0.5 cm^2 punches. Punches from site-specific dynamic field blanks were composited by site as well. At MORA, there were enough field blanks for two composites.

Each seasonal composite was extracted successively with about 170 ml each of dichloromethane (DCM), acetone, and water. The extractions were conducted at 100 °C under pressure for 30 min using an Ace 300 accelerated solvent extractor (DIONEX). The samples were evaporated using a rotavapor water bath (Büchi) and filtered through a 0.2 μm AnotopTM 10 filter (Whatman), rinsing the flask twice with 1 ml of pure solvent each time. The extract was then evaporated to ∼40 μl under ultra-high purity nitrogen. Water extracts were evaporated using a RAPIDVAP (Labconco) to 10 ml. Two ml were reserved for ion analysis and the remaining 8 ml were evaporated to 1 ml, filtered through a 0.4 μm AnotopTM 10 filter (Whatman), and evaporated under a gentle stream of nitrogen using a solvent transfer technique with methanol to ∼40 μl. Half of each solvent extract was set aside and stored in a freezer. Twenty μl of each solvent extract was spotted onto a pre-fired, pre-weighed quartz filter punch. The punches were dried in a vacuum oven (20–25 mmHg) over night at room temperature and then re-weighed to determine the mass of the residue.

The DRI filter weighing protocol conforms to the USEPA Federal Reference Method for measuring atmospheric particle mass concentration (Federal Register, 1997). Un-sampled and sampled quartz filter punches were equilibrated for at least 24 h at a relative humidity of 30–40% and a temperature of 20–23 °C. The punches were de-charged using a ^{210}Po source and weighed to 1 μg on a Cahn C-31 microbalance. Each punch was then subjected to TOR analysis to measure the OC content of the residue. The water extracts were also analyzed for chloride, nitrate, and sulfate by ion chromatography, ammonium by automated colorimetry, and sodium and potassium by atomic absorption to correct the mass of the water extract residue for inorganic mass. Measurement uncertainties were estimated from replicate analysis. For mass, pre- and post-weighing was repeated for 100% and 30% of the samples, respectively. For carbon analysis by TOR, replicate analysis was done for 10% of the samples. The concentration uncertainty (σ_C) was calculated from the paired replicate concentrations as follows:

$$D_C = \sum_{j=1}^{n} \left[\frac{|C_{j1} - C_{j2}|}{(C_{j1} + C_{j2})/2} \right] \qquad (3)$$

$$\sigma_C = C \times D_C \qquad (4)$$

where C_{j1} and C_{j2} are the first and second replicate concentrations for the jth replicate pair and n is the number of replicate pairs. D_C is generally determined for at least two concentrations ranges, e.g., high and low.

The OM/OC ratio in IMPROVE samples was inferred using a mass balance based on Eq. (1). If the reconstructed mass in Eq. (1) is reduced by the assumed OM (1.4 times OC) and augmented with ''other'', as described above and in Lowenthal and Kumar (2003), the difference between measured PM$_{2.5}$ mass and the modified reconstructed sum should in principle represent the organic mass concentration (OM). Dividing this by OC provides an estimate of the OM/OC ratio:

$$OM/OC = [PM_{2.5} - (AMSUL + AMNIT + EC + Soil + other)]/OC \qquad (5)$$

PM$_{2.5}$ sample mass and chemical concentrations at 170 IMPROVE sites from March, 1988 through May, 2003 were obtained from the VIEWS (Visibility Information Exchange Web System) web site (http://vista.cira.colostate.edu/views). Data were not available for the entire period at all sites. As noted above, IMPROVE sampling and analysis protocols are described by Eldred et al. (1998) and Malm (2000).

3. Results and discussion

3.1. Laboratory experiment

The results of the extraction experiment are presented in Table 1. Each sample composite is identified by site, season (SR = spring, SM = summer, FL = fall, WN = winter), and year. Remembering that the composited filter area for each sample was nominally 15 cm^2, the extract residue mass and OC concentrations in Table 1 are normalized to unit filter area (μg/cm^2). Analytical uncertainties for mass and OC based on replicate analysis are included in Table 1. Also shown are the corresponding bulk OC concentrations for the original samples determined by TOR. The percent OC recovery is the sum of the OC from the extracts divided by the original OC concentrations. Field blank concentrations are included at the bottom of Table 1.

Excluding one outlier with a recovery of over 1000% (INGAFL00), the average non-blank-corrected OC recovery was 115 ± 42%. While the recovery was somewhat variable, the two methods for measuring OC, i.e., TOR on the bulk aerosol sample versus TOR on solvent extracts, should not necessarily produce the same OC concentration. Most of the field blanks appeared to be grossly contaminated compared to the samples with recoveries ranging from 83.4% to 964.2%. While the field blanks were extracted and analyzed along with the ambi-

ent samples, there is no obvious explanation for how and when they were contaminated. As seen in Table 1, the first MORA field blank was the only blank with a recovery on the order of those of the samples (83.4%). We therefore used this blank to correct the samples.

It was also the case that sodium and chloride in the water extracts were contaminated by the extraction procedure. We therefore attempted to use sulfate, nitrate, ammonium, and water-soluble potassium concentrations to correct the water extract residue mass for inorganic constituents. However, we found that after the blank and ion mass correction, the mass of the water extract residue was nearly always zero or negative. Table 1 shows that for most samples, the water extract was dominated by non-carbonaceous material, probably ionic in nature. Although we attempted to correct the water extract mass for ionic concentrations, the analysis was apparently not precise enough to accomplish this. Therefore, the water extract is excluded from further consideration.

On average, DCM, acetone, and water contained 64%, 21%, and 15% of the extractable OC, respectively. Previous studies have shown that water-soluble organic carbon (WSOC) may account for over 50% of the total OC (Decesari et al., 2000). It is probable that some of the WSOC was extracted by the acetone. Average OM/OC ratios were calculated from the DCM and acetone extracts for each site and season as the OC-weighted average of the blank-corrected OM/OC ratios in the DCM and acetone extracts. Average OM/OC ratios for each site are given in Table 2. To limit the impact of experimental uncertainty on the results, samples whose OM/OC ratios were less than twice their measurement uncertainties (see Table 1) were excluded from the averages in Table 2. The results are quite self-consistent. The within-site standard deviations (expressed as coefficients of variation) range from only 8% at INGA to 19% at BIBE. The grand-average ratio is 1.92 ± 0.40. The between-site standard deviation is less than 20%. MORA showed the highest OM/OC ratios, which may be due to the opportunity for greater aging of OM collected at this remote, high altitude site. It was also the case that there was no relationship between percent recovery, as discussed above, and the DCM plus acetone ratios for individual samples (correlation = 0.008).

The OM/OC ratios for the more polar acetone extract are higher than for the less polar DCM extract for all sites. This is consistent with the assumption that the DCM extract contained less polar and less oxygenated compounds than did the acetone extract. However, it is also possible that the acetone extract contained inorganic compounds that were soluble in acetone. According to the Handbook of Chemistry and Physics (CRC, 2004/2005), (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$ are insoluble in acetone, while NH$_4$NO$_3$ is soluble to an unspecified extent. It is unlikely that the mass of the acetone extract

Table 1

Mass (MS) and organic carbon (OC) ($\mu g/cm^2$) in dichloromethane (DCM), acetone, and water extracts for sample composites and field blanks, OC on original filters, and percent recovery

Site	DCM-MS	DCM-MSU[a]	DCM-OC	DCM-OCU	ACET-MS	ACET-MSU	ACET-OC	ACET-OCU	H₂O-MS	H₂O-MSU	H₂O-OC	H₂O-OCU	∑OC$_{ext}$	Original OC	Recovery%
ACADSR98	10.59	0.63	7.99	0.76	2.25	0.59	2.16	0.21	15.87	0.79	2.87	0.27	13.03	10.15	128.37
ACADSM98	15.71	0.60	10.98	1.04	7.36	0.56	3.91	0.37	12.41	0.75	1.38	0.13	16.28	16.04	101.48
ACADFL98	8.86	0.60	6.68	0.64	7.50	0.56	3.71	0.36	87.49	0.75	12.67	1.21	23.07	11.98	192.56
ACADWN98	13.79	0.62	9.33	0.89	4.82	0.57	2.47	0.23	13.87	0.77	2.04	0.19	13.84	10.03	137.99
ACADSR99	9.28	0.56	6.41	0.61	2.36	0.56	2.08	0.20	13.75	0.75	2.86	0.28	11.35	7.87	144.26
ACADSM99	14.46	0.67	9.29	0.88	9.36	0.67	4.93	0.47	24.78	0.90	2.38	0.22	16.61	15.60	106.47
ACADFL99	6.52	0.57	5.47	0.52	3.66	0.57	2.32	0.22	18.31	0.77	3.08	0.29	10.87	9.58	113.45
ACADWN99	7.77	0.57	5.58	0.53	2.54	0.57	2.36	0.23	18.89	0.77	3.40	0.33	11.34	9.05	125.23
ACADSR00	8.09	0.59	6.10	0.58	4.70	0.59	2.39	0.23	12.45	0.73	2.21	0.22	10.70	10.70	100.00
ACADSM00	12.02	0.66	8.46	0.80	6.89	0.66	4.36	0.41	8.14	0.81	2.37	0.23	15.19	13.80	110.09
ACADFL00	5.64	0.57	4.33	0.41	3.59	0.57	2.30	0.22	7.78	0.77	2.49	0.24	9.12	9.50	95.97
ACADWN00	5.31	0.46	4.17	0.40	2.77	0.46	2.06	0.19	1.70	0.62	0.84	0.08	7.07	9.04	78.25
BIBESR98	13.17	0.76	9.25	0.88	5.20	0.76	5.18	0.49	11.52	0.86	4.11	0.39	18.54	24.43	75.89
BIBESM98	12.24	0.59	9.33	0.89	5.66	0.59	3.53	0.34	15.12	0.74	2.42	0.24	15.28	15.13	101.00
BIBEFL98	8.48	0.57	7.03	0.67	4.18	0.57	2.55	0.24	22.26	0.66	1.80	0.17	11.38	11.90	95.62
BIBEWN98[b]	8.09	0.64	5.52	0.53	4.50	0.64	2.36	0.23	9.34	0.77	1.55	0.15	9.43	8.00	117.86
BIBESR99	7.22	0.63	5.90	0.56	2.89	0.68	1.91	0.18	20.91	0.84	3.18	0.30	10.98	12.72	86.35
BIBESM99	7.68	0.79	6.21	0.60	3.54	0.85	2.63	0.25	9.51	0.79	2.01	0.20	10.85	12.00	90.44
BIBEFL99	7.18	0.55	5.59	0.53	3.94	0.59	2.78	0.27	2.75	0.97	1.87	0.18	10.24	8.03	127.50
BIBEWN99	5.26	0.55	4.43	0.42	1.19	0.59	2.29	0.22	12.04	0.70	2.40	0.23	9.12	7.70	118.45
BIBESR00	9.71	0.61	6.72	0.64	6.29	0.61	3.57	0.34	3.04	0.46	0.98	0.09	11.28	14.40	78.30
BIBESM00	8.46	0.67	5.96	0.56	4.78	0.67	2.59	0.25	3.64	0.42	0.82	0.08	9.36	9.30	100.64
BIBEFL00	3.47	0.93	5.46	0.52	5.97	0.93	4.31	0.41	4.93	0.51	0.98	0.10	10.75	8.84	121.63
BIBEWN00	8.38	1.26	7.89	0.75	5.00	1.26	4.57	0.44	3.53	0.37	0.94	0.09	13.40	7.92	169.20
GRSMSR98	11.99	0.69	8.09	0.77	10.85	0.69	6.45	0.61	18.46	0.86	2.97	0.29	17.51	23.20	75.49
GRSMSM98	14.27	0.59	9.99	0.95	15.45	0.59	7.44	0.71	3.85	0.74	1.83	0.17	19.26	28.70	67.11
GRSMFL98	11.10	0.53	7.48	0.71	10.47	0.53	5.07	0.48	6.58	0.66	2.88	0.27	15.43	23.60	65.38
GRSMWN98	13.25	0.62	10.22	0.97	5.93	0.57	3.59	0.34	23.07	0.77	5.04	0.49	18.85	18.70	100.79
GRSMSR99	15.77	0.62	11.01	1.05	10.91	0.62	5.29	0.50	NA	NA	NA	NA	NA	23.40	NA
GRSMSM99	17.68	0.58	10.84	1.03	15.44	0.58	6.63	0.63	4.57	0.79	1.54	0.15	19.01	32.00	59.41
GRSMFL99	15.59	0.72	10.36	0.99	8.62	0.77	5.78	0.55	5.04	0.97	2.51	0.24	18.65	23.10	80.73
GRSMWN99	12.75	0.52	8.72	0.83	5.85	0.56	3.62	0.35	4.82	0.70	1.84	0.17	14.18	17.90	79.21
GRSMSR00	14.00	0.34	9.02	0.86	13.21	0.37	5.94	0.57	21.95	0.46	2.05	0.20	17.02	21.50	79.14
GRSMSM00	11.69	0.31	6.71	0.64	19.83	0.34	7.54	0.72	39.95	0.39	1.44	0.14	15.69	21.60	72.64
GRSMFL00	23.50	0.38	14.59	1.39	17.11	0.41	8.69	0.83	41.69	0.51	2.94	0.28	26.22	26.20	100.08
GRSMWN00	8.78	0.28	5.88	0.56	10.05	0.30	3.80	0.36	22.65	0.37	1.71	0.16	11.40	15.78	72.21
MORASR98	7.38	0.29	4.40	0.42	2.44	0.27	1.76	0.17	10.05	0.79	1.77	0.17	7.93	9.00	88.08
MORASM98	6.16	0.28	4.27	0.41	7.34	0.29	3.04	0.29	71.87	0.75	11.62	1.11	18.93	11.10	170.54
MORAFL98	6.11	0.32	4.53	0.43	2.92	0.30	1.71	0.17	11.43	0.75	2.67	0.26	8.91	11.00	81.03

Table 1 (*continued*)

Site	DCM-MS	DCM-MSU[a]	DCM-OC	DCM-OCU	ACET-MS	ACET-MSU	ACET-OC	ACET-OCU	H_2O-MS	H_2O-MSU	H_2O-OC	H_2O-OCU	$\sum OC_{ext}$	Original OC	Recovery%
MORAWN98[b]	4.22	0.34	3.83	0.37	1.16	0.31	0.97	0.09	15.23	0.77	3.03	0.29	7.83	5.20	150.66
MORASR99[b]	4.55	0.31	3.16	0.30	1.49	0.28	1.02	0.10	4.64	0.75	1.35	0.13	5.53	6.30	87.79
MORASM99[b]	3.13	0.30	2.90	0.27	2.22	0.28	1.21	0.12	10.42	0.83	2.40	0.23	6.51	8.40	77.47
MORAFL99	5.25	0.30	4.16	0.40	3.14	0.28	1.67	0.16	5.68	0.77	1.68	0.16	7.52	8.60	87.44
MORAWN99	5.02	0.36	3.30	0.32	7.80	0.33	3.26	0.31	9.62	0.77	1.88	0.18	8.44	4.50	187.49
MORASR00	8.04	0.31	4.98	0.48	2.41	0.31	1.36	0.13	8.47	0.73	1.98	0.19	8.32	6.00	138.63
MORASM00	12.54	0.34	7.61	0.72	3.26	0.34	1.76	0.17	8.61	0.81	1.76	0.17	11.13	9.90	112.46
MORAFL00	10.46	0.27	6.39	0.61	3.60	0.27	1.85	0.18	11.81	0.77	3.07	0.29	11.30	9.10	124.16
MORAWN00	9.25	0.27	5.65	0.54	6.86	0.27	2.70	0.26	7.89	0.62	1.64	0.15	9.99	5.36	186.34
INGASR98	5.68	0.66	4.64	0.44	2.18	0.61	1.59	0.16	12.45	0.82	1.90	0.18	8.14	10.40	78.22
INGASM98	8.87	0.73	7.28	0.70	4.61	0.68	3.41	0.32	17.17	0.92	3.50	0.34	14.18	15.30	92.70
INGAFL98	9.55	0.96	6.72	0.64	4.55	0.89	2.74	0.26	26.70	1.20	4.89	0.47	14.34	12.00	119.51
INGAWN98	19.32	1.92	14.82	1.41	11.14	1.78	6.91	0.66	36.93	2.40	7.36	0.71	29.09	10.50	277.00
INGASR99[b]	7.49	0.72	5.79	0.55	1.28	0.67	2.07	0.20	14.89	0.90	2.32	0.22	10.18	9.00	113.10
INGASM99[b]	6.58	0.69	5.28	0.50	2.55	0.64	2.03	0.20	17.47	0.87	2.89	0.28	10.20	10.20	99.97
INGAFL99	12.12	0.95	8.56	0.82	2.24	0.88	1.86	0.18	18.66	1.18	3.21	0.31	13.64	11.90	114.61
INGAWN99	7.16	0.70	4.66	0.44	0.83	0.65	1.67	0.16	25.82	0.88	4.08	0.39	10.42	5.30	196.60
INGASR00	9.96	0.71	7.38	0.71	3.40	0.71	2.17	0.21	7.99	0.87	1.59	0.16	11.14	9.10	122.38
INGASM00	15.85	1.97	14.36	1.38	10.11	1.97	5.01	0.48	20.39	2.42	4.85	0.46	24.22	12.00	201.82
INGAFL00[c]	43.64	3.12	29.05	2.76	13.45	3.12	6.47	0.62	84.55	3.83	12.59	1.23	48.12	4.80	1002.46
INGAWN00	10.98	0.81	9.52	0.91	5.02	0.81	2.35	0.23	8.52	1.00	1.59	0.15	13.45	7.17	187.60

Field Blanks

Site	DCM-MS	DCM-MSU	DCM-OC	OCU	ACET-MS	ACET-MSU	ACET-OC	ACET-OCU	H_2O-MS	H_2O-MSU	H_2O-OC	H_2O-OCU	$\sum OC_{ext}$	Original OC	Recovery%
ACAD	22.00	0.78	18.55	0.88	5.64	1.56	3.78	0.36	18.95	2.22	4.32	0.42	26.64	2.76	964.23
BIBE	8.49	1.33	8.46	0.80	4.49	1.72	2.98	0.29	30.56	1.56	11.37	1.09	22.81	4.74	481.47
GRSM	9.55	1.06	7.76	0.74	2.01	1.06	1.86	0.18	22.96	1.56	2.94	0.28	12.56	3.24	388.07
MORA	3.42	0.51	3.07	0.29	0.82	0.58	1.06	0.10	11.22	0.87	2.03	0.20	6.16	7.39	83.37
MORA	14.98	0.58	11.17	1.06	24.52	0.51	8.42	0.80	25.78	0.92	3.51	0.34	23.10	3.92	589.14
INGA	12.44	1.72	10.99	1.04	2.51	1.06	2.39	0.23	9.82	1.56	1.83	0.19	15.22	5.42	280.67

[a] MSU and OCU denote mass and organic carbon analytical uncertainties.

[b] Samples with ratios less than twice their uncertainties omitted from averages.

[c] Outlier (1002% recovery).

Table 2
Weighted-average (DCM and acetone) OM/OC ratio

Site	OM/OC[a]
Acadia	1.78 ± 0.18[b]
Great Smoky Mountains	2.01 ± 0.34[b]
Big Bend	1.64 ± 0.31[b]
Indian Gardens	1.58 ± 0.13[b]
Mount Rainier	2.58 ± 0.29[b]
All	1.92 ± 0.40[c]

[a] Samples identified in Table 1 whose OM/OC ratios were less than two times their uncertainties were excluded from the site averages.

[b] Within-site standard deviation.

[c] Between-site standard deviation.

was high biased by NH_4NO_3 for several reasons. First, significant fractions of NH_4NO_3 volatilized from the quartz–fiber filter during sampling and possibly during filter storage (Hering and Cass, 1999; Ashbaugh and Eldred, 2004; Ashbaugh et al., 2004). Second, the high temperatures and vacuum applied during the extraction experiment would probably have evaporated NH_4NO_3 in the acetone extract. Finally, there was virtually no correlation ($r = 0.12$) between the mass in the acetone extract and nitrate concentration in the original samples.

3.2. IMPROVE data analysis

OM/OC ratios were calculated according to Eq. (5) for all samples with complete and nominally valid data. The uncertainty of the ratio was calculated by propagating the reported uncertainties of all measured quantities in Eq. (5) in quadrature (Bevington, 1969). To minimize the effects of measurement uncertainty on this analysis, the data were filtered according to the following two criteria: (1) $0 < OM/OC < 10$; and (2) OM/OC > three times its measurement uncertainty. The available IMPROVE data set contained 95 445 samples with nominally valid and complete data. There were 58 214 samples that met the two criteria. For the 1988–2003 period, there were roughly 1500 possible sampling periods. To estimate a grand-average ratio, only sites with at least 500 observations that met the above criteria were included. The results, representing 40 532 samples from 50 sites, are given in Table 3. The site-average ratios range from 1.34 at PUSO (Puget Sound, WA) to 3.09 at PORE1 (Point Reyes, CA), both marine sites on the west coast of the US. The average ratio over all sites is 2.07 and the between-site standard deviation is 0.32 (15%), demonstrating a high degree of consistency over the network. It should be noted that eliminating the upper limit of 10 on the ratio increases the grand average to 2.11 ± 0.37 ($N = 40 691$).

The effect of seasonal variability on the OM/OC ratio was examined by calculating site average ratios for summer (June, July, August) and winter (December, January, February). Only sites with at least 100 samples in each season were considered. Table 3 shows that the grand-average ratio for summer (2.33 ± 0.56) is higher than in winter (1.87 ± 0.35). Higher ratios during summer are consistent with the expectation that increased photochemical activity during the warmer months produces more oxidized, higher molecular weight organic compounds.

Table 3 indicates the Regional Planning Organization (RPO) for each site. The RPOs are regional entities formed to deal with regional haze issues (Watson, 2002b). Averaging the site-average ratios by RPO produces the following results: MANE-VU (2.16 ± 0.36, $N = 4$), CENRAP (2.11 ± 0.27, $N = 5$), VISTAS (2.09 ± 0.25, $N = 8$), WRAP (2.05 ± 0.35, $N = 33$). Defined as such, the OM/OC does not exhibit much geographical variability and converges on a value of about 2 across the IMPROVE network.

The accuracy of Eq. (5) may be limited by uncertainties in the assumptions underlying Eqs. (1) and (2) (Andrews et al., 2000). Potential biases may be related to estimated soil mass (Eq. (2)), retention of water by hygroscopic species when IMPROVE Teflon filters are weighed for $PM_{2.5}$ mass, the assumption that sulfate is completely neutralized as $(NH_4)_2SO_4$, and volatilization of ammonium nitrate (NH_4NO_3) from the IMPROVE Teflon filter during sampling but not from the HNO_3-denuded nylon filter on which nitrate (NO_3^-) is measured (Ashbaugh and Eldred, 2004).

In Table 4, the grand-average OM/OC ratio from Table 3 (baseline) is compared with ratios reflecting each of the potential biases discussed above. As in Table 3, only sites with at least 500 observations were included in the grand average. In Case 1, Eq. (2) was used to estimate soil mass for $PM_{2.5}$ soil composition profiles from the DRI source profile library (data available on request) representing natural soil, agricultural soil, unpaved road dust, and desert soil from studies in California, Ohio, Phoenix and Tucson, AZ, Denver, CO, Reno, NV, and the Mt. Zirkel Wilderness, CO (Chow et al., 1988, 1991a,b; Watson et al., 1988, 2000, 2001; Houck et al., 1989). The average ratio of estimated to measured soil mass was 0.91 ± 0.19, suggesting that Eq. (2) underestimates soil mass. To account for this, we divided soil mass calculated from Eq. (2) by a factor of 0.91. This decreased the grand average from 2.07 (baseline) to 2.02 (Case 1).

Case 2 examines the effect of weighing artifacts on the OM/OC ratio using the approach of Ohta and Okita (1990), Andrews et al. (2000), and Lowenthal and Kumar (2003). IMPROVE $PM_{2.5}$ mass concentrations are determined by weighing the Teflon filters from the IMPROVE sampler Module A at a nominal relative humidity (RH) of ~40%. Water uptake by soluble salts on the Teflon filter at this RH will high bias the reported

Table 3
OM/OC inferred from IMPROVE PM$_{2.5}$ and chemical concentrations

Site	Site description	State	RPO[a]	All Samples[b]			Summer[c]			Winter[c]		
				Avg.	σ[d]	N[e]	Avg.	σ[d]	N[e]	Avg.	σ[d]	N[e]
ACAD1	Acadia National Park	ME	MANE-VU	2.37	1.31	1088	2.67	1.36	345	1.97	1.00	257
BADL1	Badlands National Park	SD	WRAP	2.13	1.03	869						
BAND1	Bandelier National Monument	NM	WRAP	2.03	0.93	1011	2.15	0.90	308	1.83	0.77	212
BIBE1	Big Bend National Park	TX	CENRAP	2.30	1.10	965	2.34	1.18	235	2.28	1.00	203
BLIS1	Bliss State Park	CA	WRAP	1.80	0.74	704						
BOWA1	Boundary Waters Canoe Area	MN	CENRAP	1.98	0.87	655	2.03	0.64	211	1.94	0.91	111
BRCA1	Bryce Canyon National Park	UT	WRAP	2.29	1.10	684						
BRID1	Bridger Wilderness	WY	WRAP	2.15	1.08	664						
BRIG1	Brigantine National Wildlife Refuge	NJ	MANE-VU	1.93	1.05	831	2.34	0.92	221	1.72	1.09	212
CANY1	Canyonlands National Park	UT	WRAP	2.42	1.15	685						
CHAS1	Chassahowitzka National Wildlife Refuge	FL	VISTAS	1.76	0.76	871	2.10	0.94	202	1.54	0.50	230
CHIR1	Chiricahua National Monument	AZ	WRAP	2.54	1.31	869	2.59	1.35	283	2.48	1.22	127
CORI1	Columbia River Gorge	WA	WRAP	1.57	0.71	715	1.83	0.60	189	1.33	0.76	140
CRLA1	Crater Lake National Park	OR	WRAP	2.06	1.05	611						
DOSO1	Dolly Sods Wilderness	WV	VISTAS	2.33	1.50	924	3.49	1.82	226	1.74	1.10	217
GICL1	Gila Wilderness	NM	WRAP	2.03	0.90	571						
GLAC1	Glacier National Park	MT	WRAP	1.75	0.61	1350	1.97	0.66	358	1.58	0.45	303
GRBA1	Great Basin National Park	NV	WRAP	2.04	1.10	681	2.18	0.84	245	1.47	0.96	103
GRCA1	Hopi Point	AZ	WRAP	2.49	1.27	512						
GRSA1	Great Sand Dunes National Monument	CO	WRAP	2.23	1.13	879	2.32	0.94	319	1.69	0.85	129
GRSM1	Great Smoky Mountains National Park	TN	VISTAS	2.26	1.06	1265	2.96	1.08	355	1.80	0.96	283
GUMO1	Guadalupe Mountains National Park	TX	CENRAP	2.49	1.31	889	2.70	1.38	245	2.57	1.58	169
INGA1	Indian Gardens	AZ	WRAP	2.19	1.27	705	2.22	1.26	193	2.39	1.58	124
JARB1	Jarbidge Wilderness	NV	WRAP	2.19	0.99	659						
LAVO1	Lassen Volcanic National Park	CA	WRAP	1.84	0.81	854						
LYBR1	Lye Brook Wilderness	VT	MANE-VU	2.57	1.32	656	2.79	1.18	222	2.36	1.45	106
MACA1	Mammoth Cave National Park	KY	VISTAS	2.13	1.05	836	2.55	0.98	241	1.77	0.82	180
MEVE1	Mesa Verde National Park	CO	WRAP	2.51	1.38	783	2.34	1.20	283	2.65	1.68	109
MOOS1	Moosehorn National Wildlife Refuge	ME	MANE-VU	1.80	0.95	632	1.96	0.80	186	1.61	0.96	145
MORA1	Mount Rainier National Park	WA	WRAP	1.84	0.68	1149	1.88	0.60	294	1.83	0.64	244
OKEF1	Okefenokee National Wildlife Refuge	GA	VISTAS	1.83	0.72	1028	1.94	0.82	242	1.67	0.62	274
PEFO1	Petrified Forest National Park	AZ	WRAP	2.06	1.09	906	2.27	1.28	256	1.91	1.01	177
PINN1	Pinnacles National Monument	CA	WRAP	1.81	1.02	1099	2.04	1.21	281	1.64	0.86	251
PORE1	Point Reyes National Seashore	CA	WRAP	3.09	1.85	783	4.24	1.91	132	2.36	1.36	224
PUSO1	Puget Sound	WA	WRAP	1.34	0.68	558	1.43	0.71	116	1.41	0.80	152
REDW1	Redwood National Park	CA	WRAP	2.52	1.24	961	3.05	1.46	229	2.29	1.06	189
ROMA1	Cape Romain National Wildlife Refuge	SC	VISTAS	1.92	0.99	688	2.41	0.95	157	1.65	1.00	190
ROMO1	Rocky Mountain National Park	CO	WRAP	1.99	0.95	570						
SAGO1	San Gorgonio Wilderness	CA	WRAP	1.85	1.27	620						
SEQU1	Sequoia National Park	CA	WRAP	1.52	0.56	776	1.66	0.35	194	1.46	0.82	163
SHEN1	Shenandoah National Park	VA	VISTAS	2.46	1.31	930	3.12	1.48	311	2.02	1.14	145
SIPS1	Sipsy Wilderness	AL	VISTAS	2.01	1.03	717	2.27	0.86	218	1.84	1.27	125
SOLA1	South Lake Tahoe	CA	WRAP	1.64	0.73	703	1.72	0.74	193	1.51	0.35	145
THSI1	Three Sisters Wilderness	OR	WRAP	1.84	0.63	583						
TONT1	Tonto National Monument	AZ	WRAP	2.02	0.96	1072	2.05	0.98	289	2.00	1.06	215
UPBU1	Upper Buffalo Wilderness	AR	CENRAP	1.90	0.76	883	2.01	0.63	250	1.67	0.78	180
VOYA1	Voyageurs National Park	MN	CENRAP	1.89	0.79	576	2.08	0.75	177	1.71	0.75	117
WEMI1	Weminuche Wilderness	CO	WRAP	2.20	0.95	677						

Table 3 (*continued*)

Site	Site description	State	RPO[a]	All Samples[b]			Summer[c]			Winter[c]		
				Avg.	σ[d]	N[e]	Avg.	σ[d]	N[e]	Avg.	σ[d]	N[e]
YELL1	Yellowstone National Park	WY	WRAP	1.89	0.77	781						
YOSE1	Yosemite National Park	CA	WRAP	1.75	0.63	1054	1.83	0.51	341	1.85	1.00	115
Average				2.07	0.32[f]		2.33	0.56[f]		1.87	0.35[f]	

[a] MANE-VU (Mid-Atlantic/Northeast Visibility Union), VISTAS (Visibility Improvement State and Tribal Association of the Southeast), CENRAP (Central Regional Air Planning Association), WRAP (Western Regional Air Partnership).

[b] For sites with at least 500 samples. Total = 40 532.

[c] For sites with at least 100 winter and summer samples. Total summer (June, July, August) = 8547, total winter (December, January, February) = 6266.

[d] Standard deviation.

[e] Number of samples.

[f] Standard deviation of site averages.

Table 4
Sensitivity of OM/OC ratios to assumptions regarding Eq. (1)

Case	Overall OM/OC ratio	Number of sites in average
Baseline[a]	2.07 ± 0.32	50
1[b]	2.02 ± 0.32	49
2[c]	1.74 ± 0.30	26
3[d]	2.20 ± 0.37	51
4[e]	2.14 ± 0.32	50
5[f]	1.77 ± 0.33	28
6[g]	1.92 ± 0.31	48

[a] Follows Eqs. (1) and (2).

[b] Soil/0.91.

[c] Added water to $(NH_4)_2SO_4$ and NH_4NO_3.

[d] Substituted NH_4HSO_4 for $(NH_4)_2SO_4$.

[e] Accounts for NH_4NO_3 volatilization from Teflon filter.

[f] Combines cases 1, 2, and 4.

[g] Combines cases 1, 3, and 4 with water added to NH_4HSO_4 and NH_4NO_3.

$PM_{2.5}$ mass concentration and thus the OM/OC ratio inferred from the mass balance. When exposed to increasing RH, pure $(NH_4)_2SO_4$ and NH_4NO_3 do not begin to absorb water until the "deliquescence" RH is reached: 80% and 61% RH at 25 °C for $(NH_4)_2SO_4$ and NH_4NO_3, respectively (Kim et al., 1993). As RH decreases from above the deliquescence point, $(NH_4)_2SO_4$ and NH_4NO_3 will remain in a supersaturated solution until they crystallize at a characteristic "efflorescence" RH. The descending branch of the water growth curve is known as the "efflorescence" or "hysteresis" branch.

Experiments conducted during the Southeastern Aerosol and Visibility Study (SEAVS) and the Big Bend Regional Aerosol and Visibility Observational Study (BRAVO) revealed that deliquescence was rarely observed for ambient aerosols of complex composition (Day et al., 2000; Malm et al., 2003). We therefore estimated water uptake at 40% RH using published water activity data from the descending (hysteresis) branches of the growth curves for $(NH_4)_2SO_4$, NH_4HSO_4, and

NH_4NO_3 (Chan et al., 1992; Tang and Munkelwitz, 1994). Based on this analysis, binary solutions (salt + water) of $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3 at 40% RH contain an upper limit of 0.3, 0.3, and 0.2 g of water per gram of compound. Enhancing the $(NH_4)_2SO_4$ and NH_4NO_3 concentrations accordingly decreases the grand-average OM/OC ratio to 1.74 (Table 4). Note, however, that nearly half of the baseline sites are not represented in this average ($N = 26$). In this case, reconstructed mass was frequently greater than the measured $PM_{2.5}$ concentration, leading to many OM/OC ratios less than or equal to zero and suggesting that this scenario was not realistic, at least for those sites which were eliminated in this test. Sulfates are not always completely neutralized, especially in the eastern US during summer (Malm et al., 1991; Day et al., 1997). For Case 3, we substituted NH_4HSO_4 for $(NH_4)_2SO_4$, which is 15% heavier per mole. This increased the grand-average OM/OC ratio to 2.2 (Table 4).

IMPROVE nitrate is measured on a nylon filter preceded by a nitric acid denuder (Malm et al., 1994). Nitrate does not volatilize from this filter. Nitrate volatilization from IMPROVE Teflon filters is not measured directly and cannot be estimated without HNO_3 and NH_3 concentrations that are not measured in IMPROVE (Zhang and McMurry, 1992). Ashbaugh and Eldred (2004) estimated the maximum effect of NO_3^- volatilization on $PM_{2.5}$ concentrations in IMPROVE by assuming 100% NO_3^- losses. We adopted a more realistic approach and corrected $PM_{2.5}$ concentrations for NH_4NO_3 evaporative losses using data taken from Fig. 5 in Hering and Cass (1999). They found that, consistent with the temperature–relative humidity dependence of the $NH_4NO_3/HNO_3/NH_3$ equilibrium, NO_3^- losses were roughly 80% in summer, 20% in winter, and 40% in spring and fall in Los Angeles. Increasing IMPROVE $PM_{2.5}$ mass concentrations accordingly increased the average OM/OC ratio to 2.14 (Table 4, Case 4). All of these effects are combined in Case 5

(OM/OC = 1.77) and Case 6 (OM/OC = 1.92), with sulfate as $(NH_4)_2SO_4$ and NH_4HSO_4, respectively. Note that these potential effects are not equally probable, especially with respect to weighing artifacts and that these issues have not yet been resolved. Nonetheless, the mass balance approach points to an OM/OC ratio centered at about 2.

Perhaps the greatest uncertainty in the mass balance approach involves the measurement of OC. This problem is in part analytical because the absolute and relative concentrations of elemental and organic carbon are method dependent (Chow et al., 2001). The other important concern involves positive and negative sampling artifacts for OC (Turpin et al., 1994). As discussed above, this problem is addressed by subtracting a single quartz backup filter OC concentration to account for the positive artifact over the entire IMPROVE network. This could explain why there is such a wide range of ratios (1.3–3.1) from site to site. It reduces the confidence in the site-specific average ratios derived from the mass balance approach, but not necessarily for overall and seasonal grand averages, for which such errors should be reduced.

3.3. Reconciliation of the two approaches

A comparison between Tables 2 and 3 indicates that OM/OC ratios derived from the solvent extracts were lower than those based on the mass balance at ACAD, GRSM, BIBE, and INGA. However, this comparison involves different time periods. For a more direct comparison, average OM/OC ratios were recalculated on a seasonal basis using the mass balance approach for the five sites over the same time period as that represented by the solvent extraction experiment (1998–2000). These seasonal averages were then averaged for each site and compared with the site averages shown in Table 2. The results are presented in Table 5. The two approaches produced similar OM/OC ratios at Acadia, Great Smoky Mountains, and Indian Gardens. The ratio based on mass balance was higher than that derived from solvent extraction at Big Bend but lower at Mount Rainier. Note that the grand-average ratios for both approaches are the same (1.9). The mass balance approach is limited by the quality and completeness of the measurements.

Table 5
Comparison of OM/OC ratios from mass balance and solvent extraction

Site	Mass balance	Extraction
Acadia	2.2	1.8
Great Smoky Mountains	2.1	2.0
Big Bend	2.1	1.6
Indian Gardens	1.5	1.6
Mount Rainier	1.5	2.6
Average	1.9	1.9

As discussed above, there are a variety of assumptions and potential biases inherent in the mass balance approach that lead to a range of OM/OC ratios (Table 4). The most important of these, and the one that is almost impossible to address quantitatively, is the uncertainty of the OC sampling artifact correction. As noted above, this correction is based on a single value applied across the IMPROVE network. Again, this reduces our confidence in site-specific OM/OC rations derived from the mass balance method. However, because of the large number of sites and samples used in the mass balance, we believe that the grand averages presented in Tables 3 and 5 are more reliable.

4. Conclusions

OM/OC ratios were derived from solvent extracts of archived filter samples from five remote continental US IMPROVE sites and from a mass balance based on the difference between $PM_{2.5}$ mass and chemical concentrations of components other than organic carbon in historical IMPROVE sample data. On average, DCM, acetone, and water contained 64%, 21%, and 15%, respectively, of the extractable OC. The OM/OC ratio was lower in dichloromethane (DCM) than in acetone extracts suggesting higher ratios in more polar organic matter. The OC-weighted average of the ratios of the DCM and acetone extracts for the five sites was 1.92 ± 0.40. The average OM/OC ratio based on a mass balance from 40 532 daily IMPROVE samples at 50 sites from 1988 to 2003 was 2.07 ± 0.32. Average ratios from the mass balance were higher in summer (2.33) than winter (1.87), consistent with the expectation of more photo-oxidation of organic aerosols during the warmer months. Tests on the sensitivity of the OM/OC ratio to a variety of assumptions related to the IMPROVE mass reconstruction equation and $PM_{2.5}$ measurements leads to a range of values between 1.74 and 2.2, although the lower ratios are probably not realistic. Though the two analytical approaches were completely different in principle, they gave similar results when applied to the same sites over the same time periods. The filter extraction was not successful for the water extract, which may have contained the most polar organic compounds. Our combined results suggest that the commonly accepted value of 1.4 for the OM/OC ratio is too low and inapplicable to aerosols at remote, non-urban locations, and that a value closer to 2 seems more appropriate for remote IMPROVE locations.

approving the use of archived IMPROVE samples in this study.

References

Andrews, E., Saxena, P., Musarra, S., Hildemann, L.M., Koutrakis, P., McMurry, P.H., Olmez, I., White, W.H., 2000. Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a review of the closure between chemical and gravimetric measurements. J. Air Waste Manage. Assoc. 50, 648–664.

Ashbaugh, L.L., Eldred, R.A., 2004. Loss of particle nitrate from Teflon sampling filters: effects on measured gravimetric mass in California and in the IMPROVE network. J. Air Waste Manage. Assoc. 54, 93–104.

Ashbaugh, L.L., McDade, C.E., White, W.H., Wakabayashi, P., Collett Jr., J.L., Yu, X.-Y., 2004. Efficiency of IMPROVE network denuders for removing nitric acid. In: Proceedings, Regional and Global Perspectives on Haze: Causes, Consequences and Controversies Visibility Specialty Conference, October 25–29, 2004, Asheville, NC. Air & Waste Management Association, Pittsburgh, PA.

Bevington, P.R., 1969. Data Reduction and Error Analysis for the Physical Sciences. McGraw Hill, New York, NY.

Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Sci. Technol. 25, 221–241.

Cachier, H., Bremond, M.P., Buat-Ménard, P., 1989. Determination of atmospheric soot carbon with a simple thermal method. Tellus 41B, 379–390.

Chan, C.K., Flagan, R.C., Seinfeld, J.H., 1992. Water activities of $NH_4NO_3/(NH_4)_2SO_4$ solutions. Atmos. Environ. 26A, 1661–1673.

Chow, J.C., Watson, J.G., Frazier, C.A., Egami, R.T., Goodrich, A., Ralph, C., 1988. Spatial and temporal source contributions to PM_{10} and $PM_{2.5}$ in Reno, NV. In: Mathai, C.V., Stonefield, D.H. (Eds.), Transactions, PM_{10}: Implementation of Standards. Air Pollution Control Association, Pittsburgh, PA, pp. 438–457.

Chow, J.C., Watson, J.G., Richards, L.W., Haase, D.L., McDade, C., Dietrich, D.L., Moon, D., Sloane, C.S., 1991. The 1989–90 Phoenix PM_{10} Study. In: Vol. II: Source Apportionment. Report No. DRI 8931.6F2. Prepared for Arizona Department of Environmental Quality, Phoenix, AZ, by Desert Research Institute, Reno, NV.

Chow, J.C., Watson, J.G., Richards, L.W., Haase, D.L., McDade, C., Dietrich, D.L., Moon, D., Sloane, C.S., 1991. The 1989–90 Pilot Tucson PM_{10} Study. Vol. II: Source Apportionment. Report No. DRI 8931.8F2. Prepared for Arizona Department of Environmental Quality, Phoenix, AZ, by Desert Research Institute, Reno, NV.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in US air quality studies. Atmos. Environ. 27, 1185–1201.

Chow, J.C., Watson, J.G., Fujita, E.M., Lu, Z., Lawson, D.R., Ashbaugh, L.L., 1994a. Temporal and spatial variations of $PM_{2.5}$ and PM_{10} aerosol in the Southern California Air Quality Study. Atmos. Environ. 28, 2061–2080.

Chow, J.C., Watson, J.G., Lowenthal, D.H., Solomon, P.A., Magliano, K.L., Ziman, S.D., Richards, L.W., 1994b. PM_{10} and $PM_{2.5}$ chemical characteristics and source apportionment in the San Joaquin Valley. In: Solomon, P.A. (Ed.), Planning and Managing Regional Air Quality, Modeling and Measurement Studies. CRC Press Inc., Boca Raton, FL, pp. 687–698.

Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Merrifield, T., 2001. Comparison of IMPROVE and NIOSH Carbon Measurements. Aerosol Sci. Technol. 34, 23–34.

Countess, R.J., Wolff, G.T., Cadle, S.T., 1980. The Denver winter aerosol: a comprehensive chemical characterization. Air Pollut. Control Assoc. 30, 1194–1200.

CRC, 2004/2005. In: Lide, D. (Ed.), The Handbook of Chemistry and Physics, 85th Ed.. CRC Press, Cleveland OH.

Day, D.E., Malm, W.C., Kreidenweis, S.M., 1997. Seasonal variations in aerosol composition and acidity at Shenandoah and Great Smoky Mountains National Parks. J. Air Waste Manage. Assoc. 47, 411–418.

Day, D.E., Malm, W.C., Kreidenweis, S.M., 2000. Aerosol light scattering measurements as a function of relative humidity. J. Air Waste Manage. Assoc. 50, 710–716.

Decesari, S., Facchini, M.C., Fuzzi, S., Tagliavini, E., 2000. Characterization of water-soluble organic compounds in atmospheric aerosol: a new approach. J. Geophys. Res. 105, 1481–1489.

Eldred, R.A., Feeney, P.J., Wakabayashi, P.K., 1998. The major components of $PM_{2.5}$ at remote sites across the United States. In: Chow, J.C., Koutrakis, P. (Eds.), Proceedings, $PM_{2.5}$: A Fine Particle Standard. Air & Waste Management Association, Pittsburgh, PA, pp. 13–27.

Federal Register, 1997. US Environmental Protection Agency, 40 CFR Part 50, National ambient air quality standards for particulate matter, final rule, vol. 62, No. 138, July 18, 1997.

Grosjean, D., Friedlander, S.K., 1975. Gas-particle distribution factors for organic and other pollutants in the Los Angeles atmosphere. J. Air Pollut. Control Assoc. 25, 1038–1044.

Hegg, D.A., Livingston, J., Hobbs, P.V., Novakov, T., Russell, P., 1997. Chemical apportionment of aerosol column optical depth off the Mid-Atlantic coast of the United States. J. Geophys. Res. 102, 25,293–25,303.

Hering, S.V., Cass, G.R., 1999. The magnitude of bias in the measurement of $PM_{2.5}$ arising from volatilization of particulate nitrate from Teflon filters. J. Air Waste Manage. Assoc. 49, 725–733.

Houck, J.E., Chow, J.C., Ahuja, M.S., 1989. The chemical and size characterization of particulate material originating from geological sources in California. In: Watson, J.G. (Ed.), Transactions, Receptor Models in Air Resources Management. Air & Waste Management Association, Pittsburgh, PA, pp. 322–333.

Kim, Y.P., Seinfeld, J.H., Saxena, P., 1993. Atmospheric gas–aerosol equilibrium I. Thermodynamic model. Aerosol Sci. Technol. 19, 157–181.

Kiss, G., Varga, B., Galambos, I., Ganszky, I., 2002. Characterization of water-soluble organic matter isolated from atmospheric fine aerosol. J. Geophys. Res. 107, 8339.

Krivácsy, Z., Gelencsér, A., Kiss, G., Mézáros, E., Molnár, A., Hoffer, A., Mézáros, T., Sárvári, Z., Temesi, D., Varga, B.,

Baltensperger, P.T., Nyeki, S., Weingartner, E., . Study on the chemical character of water soluble organic compounds in fine atmospheric aerosol at the Jungfraujoch. J. Atmos. Chem. 39, 235–259.

Lowenthal, D.H., Kumar, N., 2003. $PM_{2.5}$ mass and light extinction reconstruction in IMPROVE. J. Air Waste Manage. Assoc. 53, 1109–1120.

Malm, W.C., 2000. Spatial and Seasonal Patterns and Temporal Variability of Haze and its Constituents in the United States, IMPROVE Report III. Cooperative Institute for Atmosphere, Fort Collins, CO, May 2000. Available from: <http://vista.cira.colostate.edu/improve/Publications/Reports/2000/2000.htm>.

Malm, W.C., Golestani, Y., Gebhart, K.A., Cahill, T.A., Eldred, R.A., Poirot, T., 1991. Estimation of aerosol acidity in the eastern United States. In: Proceedings of the 84th Annual Meeting of the Air & Waste Management Association, Vancouver, BC, 16–21 June.

Malm, W.C., Sisler, J.F., Huffman, D., Eldred, R.A., Cahill, T.A., 1994. Spatial and seasonal trends in particle and optical extinction in the United States. J. Geophys. Res. 99, 1347–1370.

Malm, W.C., Day, D.E., Kreidenweis, S.M., Collett, J.L., Lee, T., 2003. Humidity-dependent optical properties of fine particles during the Big Bend Regional Aerosol and Visibility Study. J. Geophys. Res. 108, 4279.

Malm, W.C., Schichtel, B.A., Pitchford, M.L., Ashbaugh, L.L., Eldred, R.A., 2004. Spatial and monthly trends in speciated fine particle concentration in the United States. J. Geophys. Res. 109, 3306.

Novakov, T., 1982. Soot in the atmosphere. In: Wolff, G.T., Klimisch, R.L. (Eds.), Particulate Carbon: Atmospheric Life Cycle. Plenum Press, New York, NY, pp. 19–41.

Novakov, T., Corrigan, C.E., Penner, J.E., Chuang, C.C., Rosario, O., Bracero, O.L.M., 1997. Organic aerosols in the Caribbean trade winds: a natural source. J. Geophys. Res. 102, 21,307–21,313.

Ohta, S., Okita, T., 1990. A chemical characterization of atmospheric aerosol in Sapporo. Atmos. Environ. 24A, 815–822.

Rogge, W.f., Hildemann, L.M., Mazruek, M.A., Cass, G.C., Simoneit, B.R.T., 1993. Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. Atmos. Environ. 27, 1309–1330.

Russell, L.M., 2003. Aerosol organic mass-to-organic carbon ratio measurement. Environ. Sci. Technol. 13, 2982–2988.

Saxena, P., Hildemann, L., 1996. Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds. J. Atmos. Chem. 24, 57–109.

Sempere, R., Kawamura, K., 1994. Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere. Atmos. Environ. 28, 449–459.

Tang, I.N., Munkelwitz, H.R., 1994. Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance. J. Geophys. Res. 99, 18,801–18,808.

Turpin, B.J., Lim, H.J., 2001. Species contribution to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass. Aerosol Sci. Technol. 35, 602–610.

Turpin, B.J., Hering, S.V., Huntzicker, J.J., 1994. Investigation of organic aerosol sampling artifacts in the Los Angeles Basin. Atmos. Environ. 28, 3061–3071.

Turpin, B.J., Saxena, P., Andrews, A., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmos. Environ. 34, 2983–3013.

USEPA, 2001. US Environmental Protection Agency Draft guidance for estimating natural visibility conditions under the Regional Haze Rule, September 27, 2001. US Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. Available from: <http://vista.cira.colostate.edu/IMPROVE/Publications/GuidanceDocs/guidancedocs.htm>.

Van Vaeck, L., Van Cauwenberghe, K., 1978. Cascade impactor measurements of the size distribution of the major classes of organic pollutants in atmospheric particulate matter. Atmos. Environ. 12, 2229–2239.

Watson, J.G., 2002a. 2002 Critical review—visibility: science and regulation. J. Air Waste. Manage. Assoc. 52, 628–713.

Watson, J.G., 2002b. Visibility: science and regulation. EM (June), 36–43.

Watson, J.G., Chow, J.C., Richards, L.W., Neff, W.D., Anderson, S.R., Dietrich, D.L., Houck, J.E., Olmez, I., 1988. The 1987–88 Metro Denver Brown Cloud Air Pollution Study. Vol. III: Data Interpretation. DRI document No. 8810.1F3, prepared for the Greater Denver Chamber of Commerce, Denver, CO, by Desert Research Institute, Reno, NV.

Watson, J.G., Chow, J.C., Kohl, S.D., Kuhns, H.D., Robinson, N.F., Frazier, C.A., Etyemezian, V., 2000. Annual report for the Robbins Particulate Study—October 1997 through September 1998. Prepared for Versar Inc., Lombard, IL, by Desert Research Institute, Reno, NV.

Watson, J.G., Chow, J.C., Houck, J.E., 2001. $PM_{2.5}$ chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in northwestern Colorado during 1995. Chemosphere 43, 1141–1151.

White, W.H., Roberts, P.T., 1977. On the nature and origins of visibility-reducing aerosols in the Los Angeles air basin. Atmos. Environ. 11, 803–812.

Zhang, X.Q., McMurry, P.H., 1992. Evaporative losses of fine particulate nitrates during sampling. Atmos. Environ. 26A, 3305–3312.